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ANOMALOUS VOLUME EXPANSION OF PLUTONIUM ALLOYS

MASTER

AUTHOR(S):

Z. Fisk, R. O. Elliott, R. E. Tate and R. B. Roof

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LOS ALAMOS SCIENTIFIC LABORATORY
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ANOMALOUS VOLUME EXPANSION OF PLUTONIUM ALLOYS

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Summary

A simple heuristic model for the valence of Pu in its various phases is used to explain the large positive deviations from Vegard's Law in α-Pu(Al), α-Pu(Ti) and δ-Pu(Sc).

Experimental Results

The effect of Al and Ti substitutions on the lattice parameters of the respective isopressed α-phase Pu alloys is shown in Fig. 1. It is known from density measurements that these solutes enter the α-phase substitutionally. The atomic volume of α-Pu is 20.0 Å^3, while those of Al and Ti are 16.6 Å^3 and 17.7 Å^3, respectively. In both cases a smaller solute causes a lattice expansion, the largest effect occurring for trivalent Al.

In Fig. 2 we show the corresponding data for α-Pu(Sc) and α-Pu(Zr). Here the atomic volumes for Sc and Zr are 25.0 Å^3 and 23.3 Å^3, respectively. The expansion is similar for both solutes, there being a slight departure from Vegard's Law.

In Fig. 3, finally, we show the large positive deviations from Vegard's Law found in δ-Pu(Sc) and α-Sc(Pu).

Valence Model

A simple qualitative model which combines valence and pressure effects provides a framework for discussing these results. We divide the 8 outer electrons of Pu into "v" valence and "f" f–electrons. We suppose that the valence electrons primarily determine the alloy chemistry of Pu. Experimental evidence favors the view that the f–electrons are delocalized. Assuming that the volume changes involved in the transitions $v \rightarrow v\pm1$, $f \rightarrow f\mp1$ are similar for 4f and 5f elements, and estimating the relative volume effects of localized versus delocalized f–electrons from the γ–α Ce transition, we conclude that the α → δ–Pu transition corresponds to $v_\delta = v_\alpha - 2$, $f_\delta = f_\alpha + 2$. Similarly, the α → ε–Pu transition corresponds to $v_\varepsilon = v_\alpha - 1$, $f_\varepsilon = f_\alpha + 1$.

The ease with which Pu appears to be able to change its f–occupancy prompts us to suppose that Pu will try to adopt a valence that corresponds to the solvent it is dissolved in. The data for α–Sc(Pu) in Fig. 3 then suggest that Pu with $v = 3$, $f = 5$ has an atomic volume of 26.3 $Å^3$. This is somewhat larger than the atomic volume of δ–Pu, and, in view of the negative thermal expansion of δ–Pu, indicates that δ–Pu has a valence slightly larger than 3. This then gives $v = 4$, $f = 4$ for ε–Pu and $v = 5$, $f = 3$, for α–Pu, the last value being close to Zachariasen's.

A trivalent impurity in α–Pu encourages neighboring Pu atoms to become trivalent. Since trivalent or "delta-like" Pu is much larger than pentavalent α–Pu, the isopressed α–Pu(Al) alloys will show large positive deviations from

Vegard's Law. The effect for α–Pu(Ti) alloys will be smaller, due to the fact that tetravalent "epsilon-like" Pu is smaller than trivalent Pu.

The anomalous expansions are not observed in α–Pu(Sc) and α–Pu(Zr). Examination of the pressure–temperature phase diagram for elemental Pu indicates that 2.5 kbar suppresses the δ phase; pressures between 3 and 20 kbar will suppress the ε phase. A large solute atom such as Sc or Zr in α–Pu will exert a pressure on neighboring Pu atoms which one can roughly estimate as of the order of tens of kilobars. This will suppress the local valence change of Pu, and we expect, therefore, a very different effect for small and large solutes. We finally note that the valence effect is again evident (where the pressure effect is absent) in δ–Pu(Sc) alloys (Fig. 3): the Sc solute atoms push neighboring Pu solvent atoms closer to $v = 3$.

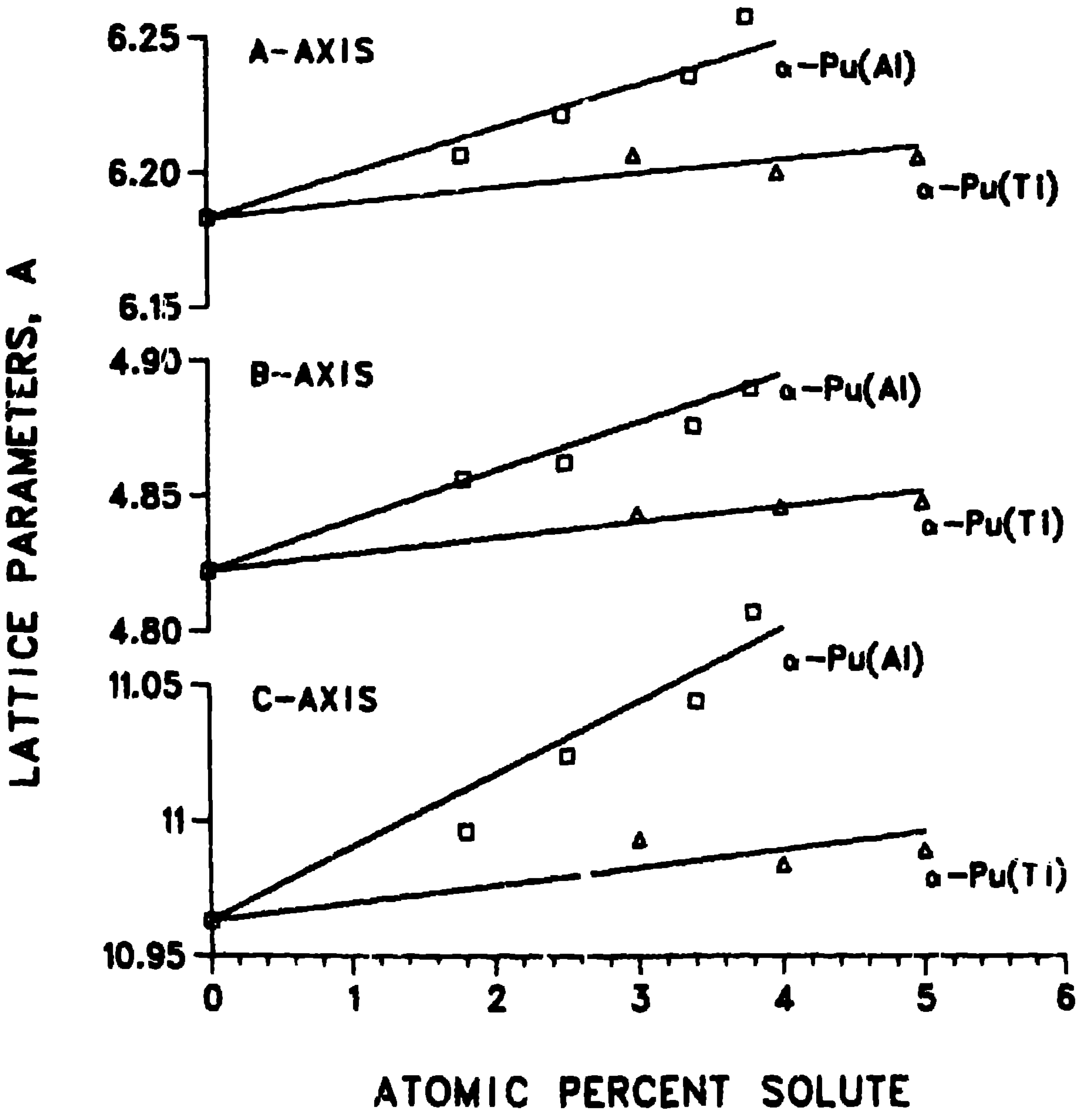

Fig. 1. Lattice parameters a, b, and c for monoclinic αPu(Al) and αPu(Tl) solid solutions versus composition.

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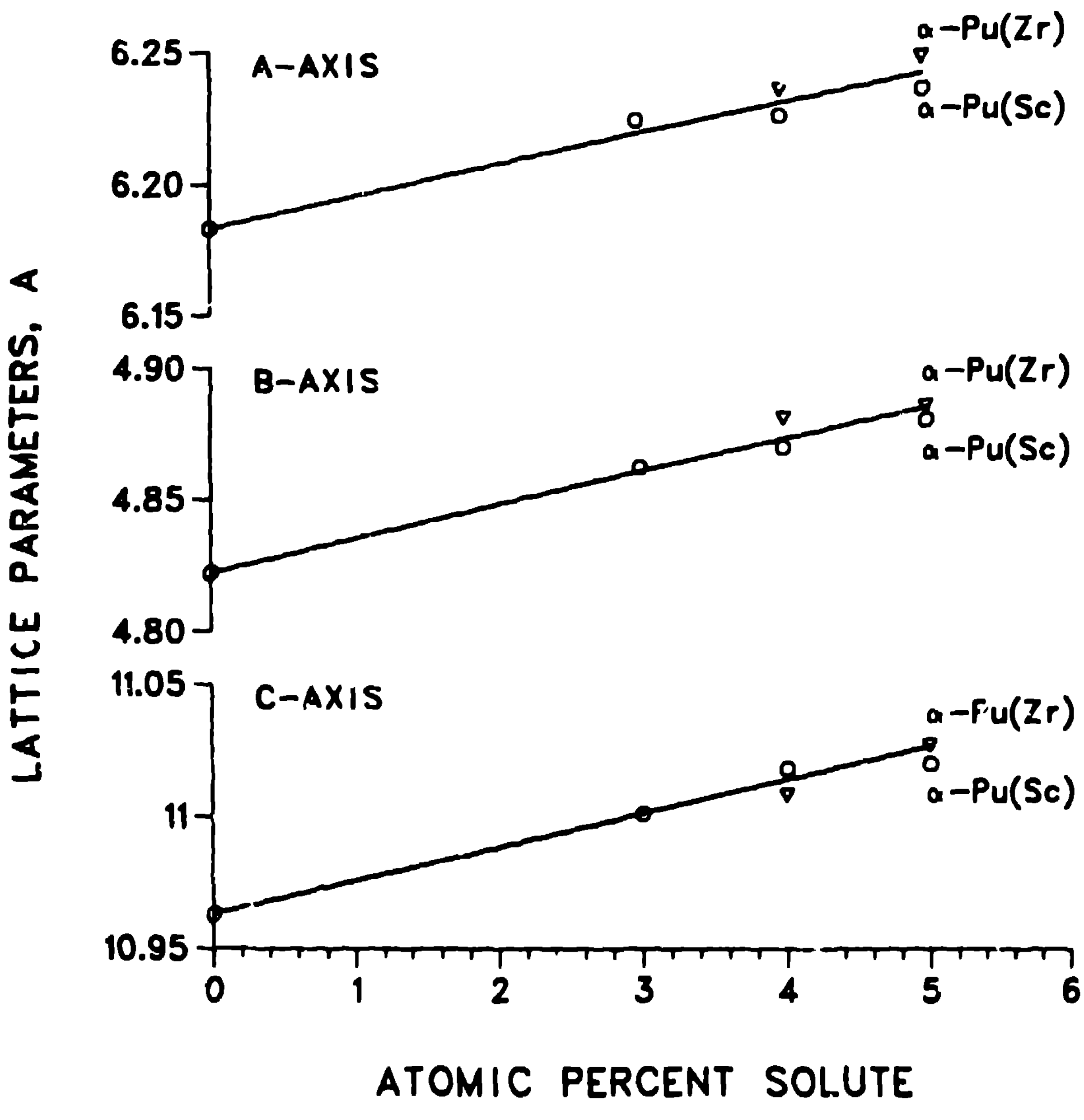

Fig. 2. Lattice parameters a, b, and c for monoclinic αPu(Sc) and αPu(Zr) solid solutions versus composition.

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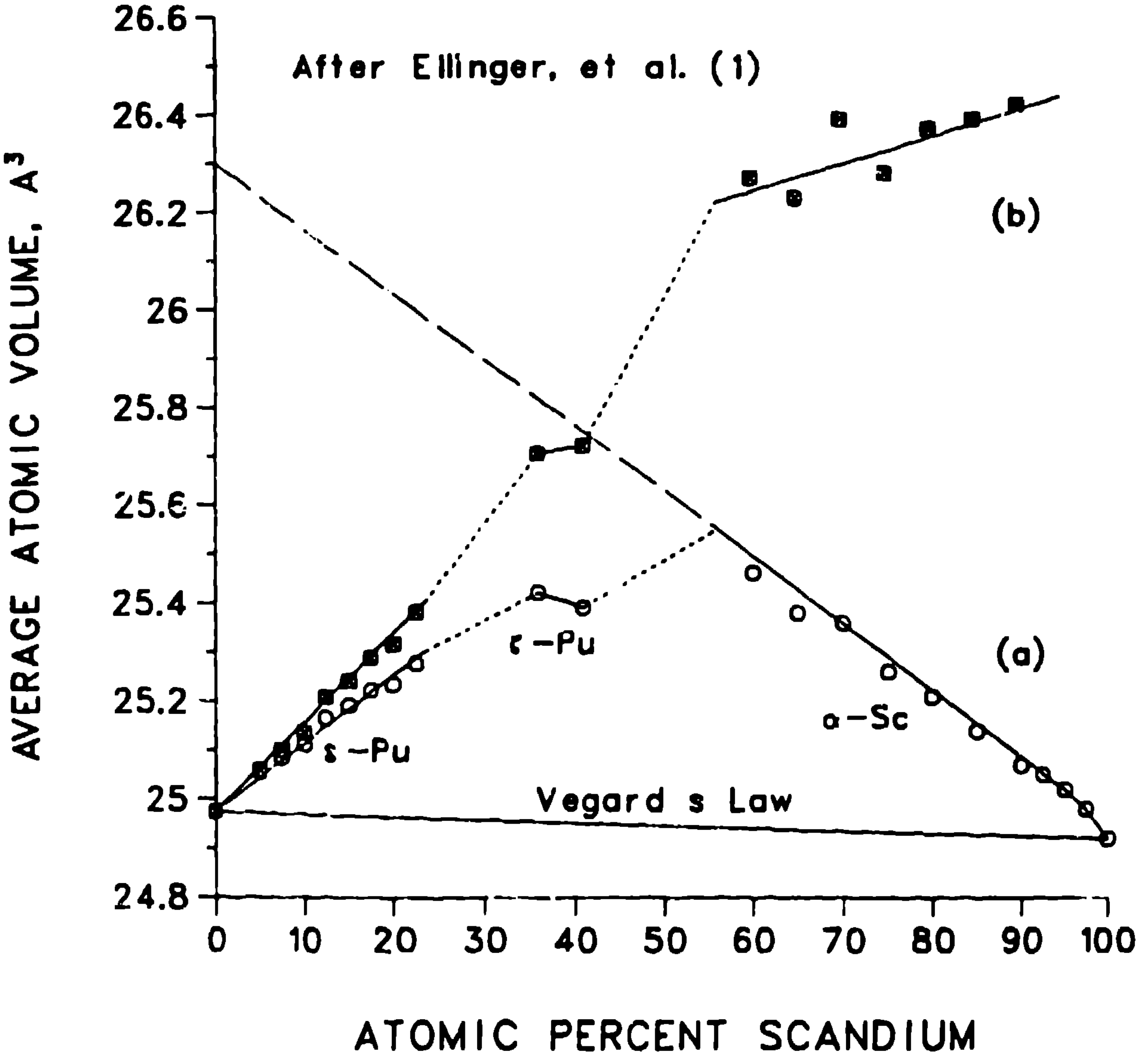

Fig. 3a. Atomic volumes as a function of composition for Pu–Sc alloys.

Fig. 3b. Volumes of the Pu atoms versus Sc content, assuming a constant volume for the Sc atoms.

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